Original

Physical and Biological Properties of Chemically Modified Wood Before and After Weathering*[1]

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Abstract——Physical and biological properties of several chemically modified woods were investigated before and after weathering. Thin wood blocks, prepared from sapwood of albizzia (*Paraserianthes falcata* Becker.) and sugi (*Cryptomeria japonica* D. Don), were treated with acetic anhydride, propylene oxide, dimethylol dihydroxy ethylene urea (DMDHEU), and low molecular weight phenol formaldehyde resin (PF-resin). Outdoor (natural) exposure was made for 1 year, and accelerated (artificial) weathering was conducted for 1,080 hours in weather-meter, by irradiation of ultraviolet ray and water flashing.

Weathering with the presence of water promoted the deterioration of wood under ultraviolet ray irradiation. From the results of color change, surface failure and weight loss of weathered specimens, acetylation and PF-resin treatments were ranked higher in protecting wood than propylene oxide and DMDHEU treatments. Enhancement of decay resistance and persistence against weathering were recognized in all treatments. The acetylation and PF-resin treatments were again better. Fast-growing and low-density albizzia may be promising for use outdoors following acetylation or PF-resin treatment.

Keywords: weathering, chemical modification, color difference, decay resistance, *Paraserianthes falcata, Cryptomeria japonica*

1. Introduction

Unprotected wood is susceptible to weathering. The consequence of weathering leads to unfavorable changes in wood, *i.e.*, discoloration, roughening and checking of surface, destruction of mechanical and physical properties, and so on. Weathering of wood is known to depend on many environmental factors. Among them, the ultraviolet (UV) component of sunlight is thought to be most responsible by depolymerizing lignin in the wood cell wall, followed by water, which washes away the degradation products, causing surface erosion.

With the recent expansion in the use of wood for outdoor applications, it is necessary to develop effective methods to avoid weather-induced deterioration. Chemical modifications have been applied to improve the weathering resistance of wood[1–5] as well as biological resistance. Although various chemical modifications have been shown to enhance the biological resistance of wood[6], few of them, such as esterification by acetic anhydride (acetylation) or etherification by butylene oxide, have been evidenced to protect well against weathering.

The first author reported previously the chemical characteristics of untreated wood exposed to weathering[7]. In the present study we examined the physical and biological properties of chemically modified wood under natural and artificial weathering conditions. For the chemical modification, acetylation as esterification, etherification by propylene oxide, crosslinking by dimethylol dihydroxy ethylene urea (DMDHEU), and impregnation of low molecular weight phenolic resin (PF-resin) were selected. Several properties of modified wood related to physical and biological properties were measured and compared before and after weathering, among methods of modifications, and between two wood species used.

2. Materials and Methods

2.1 Wood samples

Sapwood samples of 20-year-old albizzia (*Paraserianthes falcata* Becker.) and 25-year-old sugi (*Cryptomeria japonica* D. Don), 3 mm (R)×45 mm (T)×145 mm (L) in size, were prepared and oven dried at 60°C for 3 days. Ten specimens were subjected to each level of four types treatments.

2.2 Chemical modification of wood

2.2.1 Esterification by acetic anhydride (Acetylation)

Acetylation was conducted using acetic anhydride without catalyst. After vacuum impregnation with acetic anhydride, wood specimens were heated in an oven at 120–130°C for 0.5, 3 and 6 hours.

2.2.2 Etherification by propylene oxide

The treatment was made using the sufficient amount of the mixture of propylene oxide as reacting chemical and triethylamine as catalyst. They were in the ratio of 95/5 (v/v). The reaction was done in a closed reactor at 120°C for 2 hours.

2.2.3 Cross-linking by dimethylol dihydroxy ethylene urea (DMDHEU)

Liquid phase treatment with the non-formaldehyde

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agent DMDHEU was conducted. Specimens were impregnated with 5 and 10% DMDHEU aqueous solutions under occasional evacuation at room temperature and keeping for one week. The air-dried impregnated specimens were put into the glass vessel which was previously heated in an oven at 120°C. After evacuating the vessel, 4.0×10^{-3} mol/dm^3 of SO_2 catalyst was added by syringe, and the whole vessel was heated at 120°C for 24 hours.

2.2.4 Phenolic resin (PF-resin) treatment

Wood specimens were impregnated with 7.5% and 10% aqueous solution of PF-resin having average molecular weight of 334 under reduced pressure for 1 hour and keeping in atmospheric pressure for 1 day. The impregnated specimens were air-dried for 3 days. The specimens were heat-cured by raising the temperatures to 60, 80, 100, 120, 140, and 150°C for 2 hours at each step to insure the polymerization of the resin. All treated specimens were thoroughly rinsed in running water for 10 days to leach out the unreacted chemical agents.

2.3 Weathering of wood specimens

2.3.1 Natural weathering

Treated and untreated specimens were exposed to natural weathering with inclination at an angle of 45 degrees for one year (November 1994 to October 1995) on campus at the Wood Research Institute, Kyoto University, Uji-City, Kyoto Prefecture, Japan (135°48′E, 34°54′N). The average temperature, total rainfall and amount of sunshine in the test site during the exposure period was 15.9°C, 1,358 mm and 1,713 hours, respectively (Amedas Information, 1994, 1995).

For natural weathering with rainfall, the specimens were placed outside without any covering. For natural weathering without rainfall, the specimens were exposed on sunny days but shaded by a glass cover when it rained. Three specimens of each level of 4 types of the treatments were exposed.

2.3.2 Artificial weathering

Accelerated weathering was carried out using a commercial chamber machine, the Sun-Shine Super Long-life Weather Meter WEL-SUN-HC (Suga Test Machine Co., Ltd. Tokyo, Japan), which can be controlled for both light irradiation and water. Specimens were exposed to a 3-kWh carbon arc light through a glass-filter that cuts off light below 255 nm. The chamber was kept at 50°C and 50% relative humidity for 1,080 h. Distilled water was flashed for 12 min each hour. The temperature of the black-panel was kept at 63°C. Three specimens of each level of 4 types of the treatments were exposed.

2.4 Measurements of related properties of wood through chemical modification and weathering

2.4.1 Weight gain by treatment

The percent weight gain (WG) was obtained from weights before and after the treatments according to the following formula:

$$WG\,(\%)=\frac{W_2-W_1}{W_1}\times100 \qquad (1)$$

where W_1 is the dry weight of a specimen before treatment and W_2 that after treatment.

2.4.2 Determination of color difference during weathering

The color change was determined at three locations of the surface of each specimen by using Color Difference Meters of Z-1001 DP (Nippon Denshoku Kogyo Co., Ltd.) for natural weathering, and TOP-scan TC-1800MK-II (Tokyo Denshoku Co., Ltd.) for artificial weathering. The average color difference (ΔE^*) was calculated from the value of L^* (lightness), a^* (red to green along the X-axis) and b^* (yellow to blue along the Y-axis) color parameters at each location on the samples before and after weathering using the following equation.

$$\Delta E^*=\sqrt{(L_x^*-L_0^*)^2+(a_x^*-a_0^*)^2+(b_x^*-b_0^*)^2} \qquad (2)$$

L_x^*, a_x^*, b_x^* are the average color measurement at time x, and L_0^*, a_0^*, b_0^* are the average color measurement at time 0.

2.4.3 Visual inspection of surface appearance during weathering

The extent of surface cracking and checking in specimens was separately rated visually as follows:

0 - No sign of cracking (checking)
1 - Cracking (checking) occurred at less than 10% of surface area
2 - Cracking (checking) occurred at 10–20% of surface area
3 - Cracking (checking) occurred at 20–40% of surface area
4 - Cracking (checking) occurred at 40–60% of surface area
5 - Cracking (checking) occurred at more than 70% of surface area

In this inspection, the surfaces of each specimen were sectioned into one centimeter squares, and the numbers of squares with more than one crack or check were counted to calculate the proportion of the total number of squares. These two ratings were added together to give a total weathering index (WI). In addition, the specimens, exposed to weathering, were weighed to calculate the weight loss after weathering.

2.4.4 Weight loss during weathering

The percent weight loss (WL) of each specimen during weathering was calculated as follows:

$$WL=\frac{W_1-W_2}{W_1}\times100 \qquad (3)$$

where W_1 is the dry weight of specimens before and W_2 that after weathering.

2.4.5 Evaluation of decay resistance

Before and after exposure to natural and artificial weathering, specimens were cut into blocks 22.5 mm (T) × 24 mm (L) in size, and then subjected to a decay test according to JWPA (Japan Wood Preserving Association) standard No. 3, 1992. Three treated or untreated wood blocks were placed on a mat of the test fungus in a glass jar. A monoculture decay test was conducted for 8 weeks at 28°C using a brown rot fungus, *Fomitopsis palustris* (Berk. et. Curt.) Gilbn. & Ryv. and a white rot fungus, *Trametes versicolor* (L.: Fr.) Pilát. After the adherent mycelia were cleaned off, the weight of the blocks was measured, and weight loss (WL) was calculated on the basis of their oven dried weights before and after the decay test.

3. Results and Discussion

3.1 Weight gain due to treatment

Average WGs in each treatment are shown in Table 1.

Table 1. Average weight gain of albizzia and sugi wood after treatment.

Treatment	Reaction time (hr)	Weight gain (%)	
		Albizzia	Sugi
Acetic anhydride	0.5	14.4	17.1
	3	18.4	22.6
	6	19.7	24.8
Propylene oxide	2	5.1	7.1
DMDHEU (5%)	24	6.7	12.2
(10%)	24	19.7	22.6
PF-resin (7.5%)	12	7.2	16.7
(10%)	12	16.0	20.6

Note: Average of 10 specimens.

The WGs increased with the increase of agent concentration or reaction time. Although both wood species have almost equal specific gravities, WGs of sugi wood were greater than those of albizzia in all treatments used. This might be due to the specific anatomical structure of each species which lead to different penetration of chemical reagent.

3.2 Color difference

Through acetylation and propylene oxide treatment, specimens became yellowish. The PF-resin and the DMDHEU treated specimens changed from brown to dark brown.

The color changed in proportion to the exposure time under all weathering conditions. Therefore, the results shown in Figs. 1–3 are for 6 and 12 months of natural weathering and 600 and 1,080 hours of artificial weathering.

The results clearly showed that color change was prominent for untreated and treated specimens under natural weathering with rainfall and artificial weathering with water flashing (Figs. 1 and 3). However, when exposed to natural weathering with sunlight only, all specimens suffered less color change than under other weathering conditions (Fig. 2). As reported previously, the presence of water possibly promoted the weathering

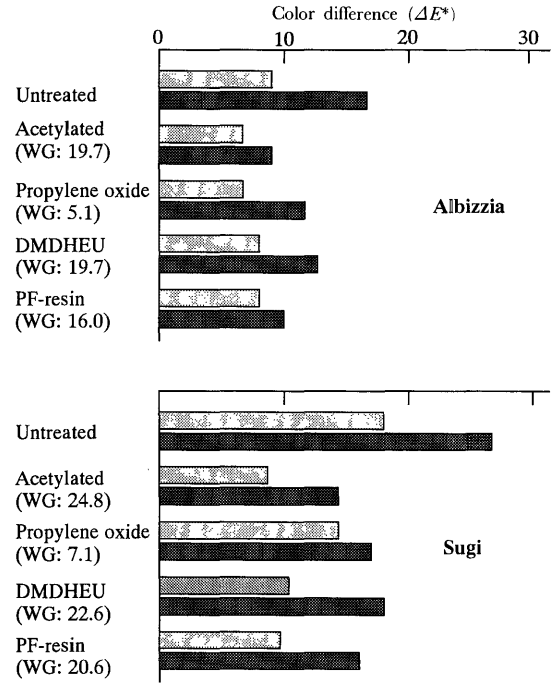

Fig. 2 Change in color of outdoor weathered wood (without rainfall). Exposure time: 6 months, 12 months.

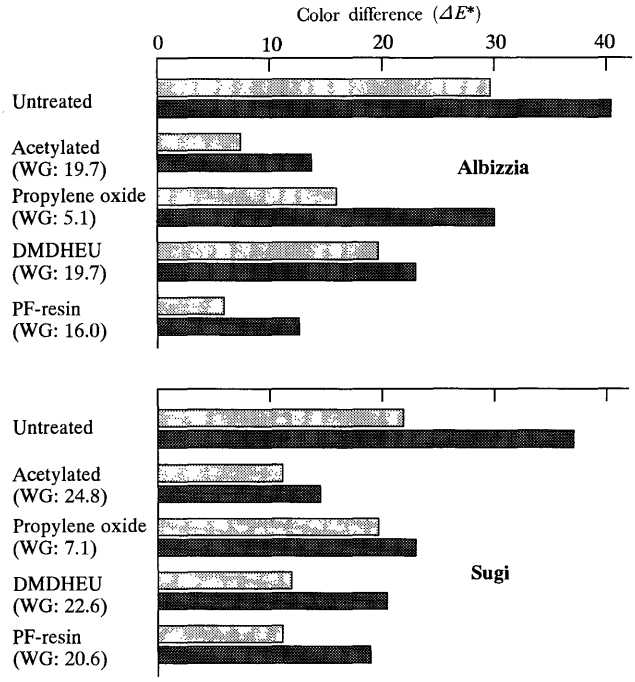

Fig. 1. Change in color of outdoor weathered wood. Exposure time: 6 months, 12 months.

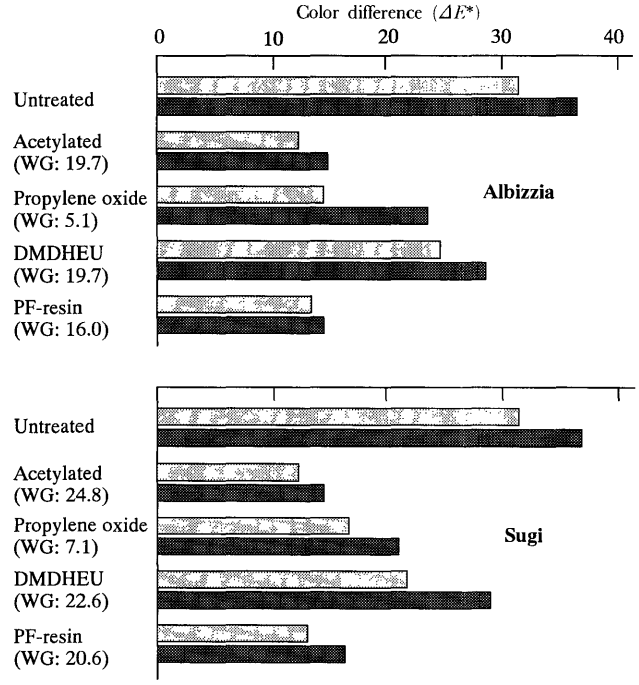

Fig. 3. Change in color of artifical weathered wood. Exposure time: 600 h, 1,080 h.

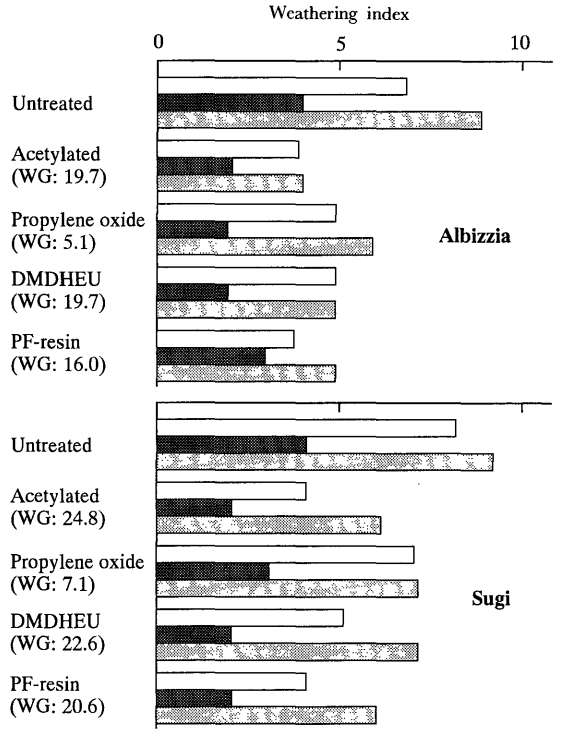

Fig. 4 Surface appearance of chemically modified wood exposed to weathering. Note: Weathering index is the sum of the extent of cracking (0–5) and checking (0–5). ☐ Natural weathering, ■ Natural weathering without rainfall, ▒ Artificial weathering.

deterioration of wood under UV irradiation[7].

Color changes were reduced by treatment, but the effect varied with the method of the treatment. Acetylation and PF-resin impregnation was better than DMDHEU and propylene oxide treatments in minimizing the color change of specimens. According to a report by Kiguchi[5], the phenolic hydroxyls in lignin were probably much substituted by acetyl or phenol resin groups during treatment. This might result in the lesser formation of radicals by UV irradiation to yield colored quinone structures.

3.3 Surface deterioration and weight loss after weathering

Visual assessments of the surface appearance of weathered specimens are shown in Fig. 4 as a weathering index (WI). Weight loss values for weathered specimens are shown in Tables 2 and 3. Natural weathering without rainfall yielded less weathering deterioration than did the other two conditions with water, showing a smaller value of WI and WL. As reported earlier[8–10], the roughening and checking of the exposed surface is normally accelerated by the leaching of low molecular weight degradation products of lignin.

Weight loss of weathered specimens might be mainly due to the formation of water-soluble products in addition to gaseous and volatile products[11,12]. Under natural weathering conditions, weight loss might be partly due to microbial attack which was not observed in artificial weathering. However, the consistently higher values of WI and WL for artificial weathering might be due to some

Table 2. Weight loss of chemically modified albizzia wood under three weathering conditions.

Treatment	Weight gain (%)	Weight loss (%)		
		Natural weathering[a]	Natural weathering without rainfall[b]	Artificial weathering[c]
Untreated	0	13.1	6.0	16.7
Acetylation	14.4	6.9	3.9	13.7
	19.7	5.6	3.6	10.0
Propylene oxide	5.1	9.7	5.2	14.7
DMDHEU	6.7	10.8	5.1	15.0
	19.0	9.0	5.9	13.8
PF-resin	7.2	7.8	4.2	12.6
	16.0	5.2	4.0	11.7

Note: Average values of 3 specimens. [a] After 1 year, [b] After 1 year, [c] After 1,080 h.

Table 3. Weight loss of chemically modified sugi wood under three weathering conditions.

Treatment	Weight gain (%)	Weight loss (%)		
		Natural weathering[a]	Natural weathering without rainfall[b]	Artificial weathering[c]
Untreated	0	14.1	6.5	16.4
Acetylation	17.1	8.4	4.2	13.6
	24.8	5.1	3.0	9.2
Propylene oxide	7.1	9.7	5.2	14.1
DMDHEU	12.2	11.4	5.5	14.0
	22.6	13.1	4.5	13.1
PF-resin	16.7	7.4	3.9	11.4
	20.6	4.5	3.1	8.9

Note: See Table 2.

Table 4. Weight loss of albizzia wood due to decay before and after weathering in an 8-week laboratory test.

Treatment	Weight gain (%)	Weight loss (%)[a]					
		Fomitopsis palustris			*Trametes versicolor*		
		Before exposure	After exposure		Before exposure	After exposure	
			Natural weathering[b]	Artificial weathering[c]		Natural weathering[b]	Artificial weathering[c]
Untreated	0	46.7	49.8	58.7	42.0	54.2	63.2
Acetylation	14.4	1.7	1.7	7.6	0	0.7	0.7
	18.4	1.0	3.8	—	0	0.2	2.2
	19.7	0	0.4	0.6	0	0.7	1.2
Propylene oxide	5.1	9.6	21.8	27.6	8.8	15.2	22.1
DMDHEU	6.7	2.0	3.9	11.6	2.6	2.9	8.2
	19.0	0.4	2.6	4.2	1.2	1.7	3.7
PF-resin	7.2	7.9	13.8	18.7	6.2	11.2	19.8
	16.0	3.4	10.8	18.0	3.9	9.0	13.6

[a] Average value of 9 specimens, [b] Natural exposure for 1 year, [c] Artificial exposure for 1,080 h.

Table 5. Weight loss of sugi wood due to decay before and after weathering in an 8-week laboratory test.

Treatment	Weight gain (%)	Weight loss (%)[a]					
		Fomitopsis palustris			*Trametes versicolor*		
		Before exposure	After exposure		Before exposure	After exposure	
			Natural weathering[b]	Artificial weathering[c]		Natural weathering[b]	Artificial weathering[c]
Untreated	0	43.0	55.9	59.0	40.9	50.1	56.7
Acetylation	17.1	0	5.4	13.6	0	3.7	10.3
	22.7	0	0	0.3	0	1.7	6.0
	24.8	0	0	0	0	0.5	8.0
Propylene oxide	7.1	10.6	20.9	32.1	5.3	11.6	29.7
DMDHEU	12.2	4.6	5.2	11.2	3.1	4.0	9.3
	22.6	2.9	4.2	6.2	2.1	2.9	7.4
PF-resin	16.7	0	2.4	2.9	0.8	1.9	2.9
	20.6	0	0	1.9	0	0.3	0.9

Note: See Table 4.

unknown factors or excessive actions of UV and water on outdoor exposure for more than one year.

3.4 Decay resistance

Weight loss (WL) by decay in untreated and treated woods is shown in Tables 4 and 5. With treatment, WLs decreased markedly in both wood species exposed to test fungi. Propylene oxide treated wood showed the greatest WL, but this is probably due to the lower WG in the present study. These results with non-weathered chemically modified wood were similar to those reported previously[6].

A comparison of the biological resistance of treated wood before and after weathering is considered a useful way to evaluate performance under severe conditions because the deterioration of mechanical and physical properties of weathered wood is mostly attributed to the degradation of wood components by non-biological and biological agents. After weathering, untreated wood was attacked to a greater extent than before weathering. A reduction of lignin and the occurrence of surface failure probably promoted the fungal activity.

Artificial weathering caused greater WL by decay than natural weathering. This is probably related to the more extensive destruction and degradation of specimens exposed to artificial weathering (Fig. 4 and Tables 2 and 3).

With a few exceptions, notably wood specimens with low WGs, chemically modified woods could tolerate fungal attack after severe weathering. In particular, acetylated albizzia with 19.7% WG and PF-resin treated sugi with 16.7% and 20.6% WGs, showed less than 3% WL on exposure to both decay fungi, after natural and artificial weathering. A less than 3% WL is designated as the performance requirement of the JWPA standard for a 'good' decay resistant material or good preservative.

4. Conclusion

The physical and biological properties of chemically modified wood were investigated under natural and artificial weathering conditions.

From the results of color change, surface failure and weight loss of weathered specimens, it was concluded that the presence of water promoted the deterioration of wood under UV irradiation. The four treatments tested yielded significant protective effects against weathering. Among them, acetylation and PF-resin treatments were ranked higher than propylene oxide and DMDHEU treatments.

Enhancement of decay resistance and persistence against weathering were observed in all treatments. Acetylation and PF-resin treatments were again ranked higher, since they yielded low WL values, less than 3% which is the performance requirement of the JWPA standard for decay resistant wood material.

Fast growing and low density albizzia wood is considered promising for use outdoors following acetylation or PF-resin impregnation.

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